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Project Summary

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Organic Chemical Fate Prediction in Activated Sludge Treatment Processes

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This project summary describes results from a broadly based effort to determine the feasibility of predicting the fates of organic chemicals in diffused air, activated sludge wastewater treatment processes. The three conversion/removal mechanisms emphasized in this work were stripping, sorption on biomass, and bio-oxidation (biotransformation and mineralization). After an initial literature review and critique, separate projects were implemented to study experimental and mathematical predictive methods on each individual fate mechanism and to develop experimental and/or mathematical protocols where needed. Finally, a project was implemented to couple the mechanisms in a semi-deterministic predictive equation and to attempt initial verification for the equation in a continuous, completely mixed laboratory activated sludge study.

Specific compounds studied in this project include methyl ethyl ketone, toluene, phenol, aniline, 1,4-dichlorobenzene, 2,4-dichlorophenol, and pentachlorophenol. Only certain compounds typical for the mechanism of interest were studied in each mechanism project. Both ^{14}C-labeled and nonlabeled compounds were used in the sorption, bio-oxidation, and laboratory activated sludge projects to provide independent and corroborative analysis as well as an unambiguous measure of bio-oxidation mineralization.

Stripping studies in a coarse bubble diffuser reactor determined the kinetic relationships between compound Henry's law constants, liquid volume, and air flow rate and the effects of contaminants on stripping kinetics. Sorption studies used nonviable biomass in a special variable-volume reactor to measure sorption equilibria and to estimate sorption kinetics. Predictive equations are proposed for stripping and sorption processes.

Bio-oxidation kinetics for both biotransformation and mineralization were determined for batch, fill-and-draw, and continuous systems. First-and second-order (first-order in both substrate and biomass concentrations) kinetics were formulated. Specific degrader and total viable subpopulations were enumerated.

An algebraic, coupled, predictive equation and related fate equations are proposed for diffused air, completely mixed activated sludge systems. Unverified examples of the use of these equations for fate prediction are also presented.

This Project Summary was developed by EPA's Water Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The goal of this research was to evaluate the potential of developing a method for quantitatively predicting the fates of chemicals in an activated sludge plant—a predictive fate method (PFM). For PFM development, the theory behind the specific transport and conversion mechan-

isms must be known and these mechanisms must be coupled into a combined, dynamic model. Experimental data must exist or be generated on each mechanism to evaluate and verify the model. Collection of these data must be controlled so that the effects of different mechanisms can be analyzed separately. The model or method must be extensively tested, ultimately against full-scale data.

This project was conceptualized with the following objectives:

1. To survey and assess the existing data base related to stripping, biomass sorption, and bio-oxidation mechanism rate predictions.
2. To select a limited list of compounds for study that might be indicative of the behavior of many more organic compounds.
3. To develop experimental protocols to measure and quantify the kinetics of stripping, sorption onto biomass, and bio-oxidation.
4. To develop mathematical protocols or models to describe the removal/conversion rates for the stripping, sorption, and bio-oxidation mechanisms.
5. To develop an overall experimental protocol for measuring the mechanism kinetic rates in a continuous system more representative of real operating activated sludge plants.
6. To develop an overall mathematical protocol or model to incorporate the individual mathematical predictors and describe compound fates in a complex system indicative of an operating activated sludge plant.
7. To determine the feasibility of evaluating the kinetic rate and other constants necessary for individual or coupled mechanism fate prediction from physical, chemical, or structural properties of the compound itself.

The literature was surveyed to determine the present level of understanding of the relationships between chemicals and their treatment in activated sludge treatment processes. Treatability was analyzed in terms of the basic removal/conversion mechanisms of (1) bio-oxidation, (2) stripping, and (3) sorption. In some cases, other mechanisms such as chemical oxidation, hydrolysis, or photolysis become important. The first three mechanisms were given priority in this study.

Selection criteria were developed and applied to a large list of aromatic compounds resulting in a limited set of compounds that potentially represented a wide range of variation in each removal mechanism.

Compounds ultimately studied in this project are:

- Stripping: toluene, 1,4-dichlorobenzene, methyl ethyl ketone, phenol
- Sorption: phenol, 1,4-dichlorobenzene, pentachlorophenol
- Bio-oxidation: phenol, toluene, aniline, 2,4-dichlorophenol (very limited testing)
- Laboratory scale activated sludge: phenol, toluene, aniline, pentachlorophenol (biological rates minimized)

A waste stream was selected that possessed time based uniformity. Pulp and paper mill foul condensate is a distillate of the liquor from the pulping process and is relatively uniform in composition over time. The focus of this study was to determine methods to predict fates of organic compounds added to this wastewater, not to determine the treatability of a specific industrial waste stream.

Biologically inactive (nonviable) biomass was required for conducting experiments on the biological sorption of organics. Five techniques were tested: gamma irradiation, formaldehyde treatment, lyophilization, lyophilization followed by dry heating, and lyophilization followed by exposure to UV light. Biomass from the acclimation reactors was used in all experiments. Of the methods tested, the most desirable was lyophilization of activated sludge followed by dry heating at 105°C for 3 hours. This method produced a stable, dry product that upon rehydration retained the physical flocculation and settling properties of the viable biomass and appeared to have a long shelf life.

Stripping, sorptive, and bio-oxidative fates of the test chemical of interest were determined for batch, fill-and-draw, and continuous laboratory-scale activated sludge (LAS) reactor conditions. Conventional analytical techniques using chromatographic procedures and radiochemical tracers were used to determine influent and effluent chemical concentrations, fractions of sorbed and stripped chemicals, and biological degradation and transformation products including CO_2.

Stripping Predictive Fate Method Results

Stripping tests were conducted with experimental equipment as shown in Figure 1. The system's liquid volume was about 26 L, and air flows from 2 to 8 L/min were used. The stripping PFM developed offers a simpler approach for estimating stripping rates in clean water and wastewater than other approaches based on the two-film theory of mass transfer. This method incorporates the Henry's law constant (H_c in torr L/g-mole) and the liquid volume-to-air flow ratio (V/Q_{air}) to directly yield the stripping rate constant ($K_a{}^{st}a$) for clean water systems. Equations predicting the stripping rate constant from the compound Henry's law constant follow the form of $K_a{}^{st}a \cdot V/Q_{air} = 3.71 \times 10^{-3} (H_c)^{1.045}$ for a clean water system. Units are hr^{-1} for $K_a{}^{st}a$ and hr for V/Q_{air}. When the dimensionless Henry's law constant (H_i) is used, the dimensionless equation, $K_a{}^{st}a \cdot V/Q_{air} = H_i$, is developed. This result, along with other studies in this area, strongly suggest that the process of stripping from coarse bubble diffuser systems is a single-stage equilibrium process.

The presence of surfactants, salts, oils, and nonviable biomass was found to vary the stripping rate, but in no case was the effect more than 50% when compared with that of clean water. The effect seemed to be the strongest for the higher volatility compounds.

The values of the stripping rate constant, $K_a{}^{st}a$, predicted from the model developed in this study, seem to agree reasonably well with previously reported values. This suggests the possibility of application beyond the compounds studied herein.

The stripping PFM was tested in continuous LAS units. The measured toluene stripping rate was found to be consistent with the predicted toluene stripping rate constant. This further substantiates that the stripping PFM may be useful for prediction of compound stripping in continuous "real world" systems.

Biomass Sorption Predictive Fate Method Results

Sorption experiments were conducted to determine sorption kinetic rate constants and equilibrium relationships between aqueous phase concentration and loadings onto biological solids for three test compounds. Test compounds were chosen to span a wide range in potential for sorption as indicated by the octanol-water partition coefficient (K_{ow}). Compounds that were studied include phenol (K_{ow} = 31), 1,4-dichlorobenzene (K_{ow} = 2455), and pentachlorophenol (associated form, K_{ow} = 132,000; dissociated form at pH = 7, K_{ow} = 7,700). All octanol-water

partition coefficients in this summary are unitless ratios of equilibrium compound concentrations in the octanol and water phases.

Tests with phenol and 1,4-dichlorobenzene indicate that equilibrium was reached in less than 15 minutes. Pentachlorophenol sorption appears to follow a two-step process, with a very rapid initial sorption step and subsequent slower approach to equilibrium.

For batch testing where sorption is the sole removal mechanism, the equilibrium aqueous concentration and substrate loading on biomass may be expressed:

$$Cae = \frac{C_{ao}}{(K_{ow} X f_L / 1000 \rho_L) + 1}$$

$$C_s = \frac{C_{ao}}{(X/1000) + (\rho_L / K_{ow} f_L)}$$

where:

C_{ae} = equilibrium aqueous phase substrate concentration ($\mu g/L$)

C_s = solids loading on biomass ($\mu g/g$)

C_{ao} = initial aqueous phase substrate concentration ($\mu g/L$)

K_{ow} = unitless concentration ratio octanol/water partition coefficient

X = solids (biomass) concentration (mg/L, dry basis)

f_L = lipid weight fraction of biomass

ρ_L = lipid density (g/L)

Table 1 presents a summary of the measured and predicted endpoint (equilibrium) values of C_{ae} for the sorption experiments. Table 2 presents measured and predicted percent removals calculated from data in Table 1 and the starting concentrations. Table 3 presents measured and predicted loadings (C_s).

Generally, good agreement is seen between measured and predicted values. Exceptions occur for experiments SP-1 and 2, the start-up experiments, and SP-6 where the mixing intensity was reduced and the experiment was run at 4°C.

Bio-oxidation Kinetic Measurements

The contribution of bio-oxidation to predictive fate assessment of organic pollutants in industrial waste treatment was determined for batch, fill-and-draw, and continuous LAS bioreactors. Bio-oxidation of specific pollutants was measured in activated sludge samples under batch assay conditions. Mineralization (oxidation to CO_2) of ^{14}C-labeled pollutants was chosen as a primary and unambiguous measurement of bio-oxidation.

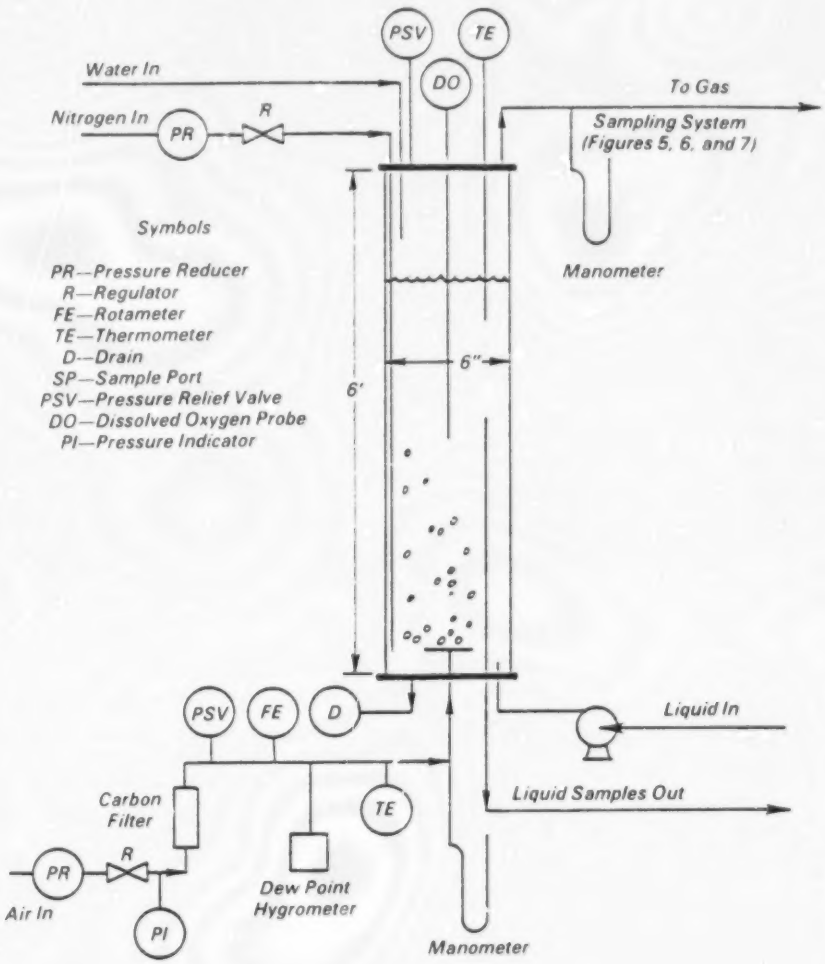

Figure 1. Apparatus Used in the Stripping Experiments

Qualitative and quantitative measurements of specific degradative bacterial populations comprising the activated sludge were performed. These measurements and associated enzymatic activites were used to evaluate the potential for describing bio-oxidation kinetics as a function of the biological community. In addition, the potential for predicting qualitative and quantitative pollutant fate relative to sludge composition and activity was investigated.

Laboratory-Scale Activated Sludge Study

The purpose of this study was to quantify the removal mechanisms of four organic substrates in continuous flow, completely mixed activated sludge units. Two 11-L LAS units were operated at mean cell residence times of approximately 5 and 10 days. These data were to be used to test the predictive fate methods that had previously been developed for stripping, sorption, and bio-oxidation.

Material balances around the activated sludge units revealed that the fate of phenol and aniline are almost identical, with >99.8% of the parent compound bio-

Table 1. Comparison of Measured and Predicted Sorption Endpoint Concentrations for Batch Experiments

Compound	Experiment	Measured Concentration (mg/L)	Predicted Concentration[a] (mg/L)	Percent[b] Deviation
Phenol	SP-3	73.0	74.2	-1.6
	SP-4	73.3	74.6	-1.8
	SP-5	71.8	72.8	-1.4
	SP-6	76.8	75.7	1.4
1,4-Dichlorobenzene	SP-1	26.6	17.8	33.0
	SP-2	54.2	33.8	37.6
	SP-10	13.9	14.3	2.9
	SP-11	2.7	3.5	-29.6
Pentachlorophenol[c]	SP-7	0.8	0.91	-13.8
	SP-8	1.5	1.22	18.7
	SP-9	0.3	0.78	-160
	SP-11	0.7	0.99	-41.4

[a]Where $f_L = 0.2$ and $\rho_L = 900$ g/L.
[b]Percent deviation = (measured value - predicted value) ÷ measured value x 100.
[c]Pentachlorophenol partially ionized at pH = 7, $K_{ow} = 7700$.

Table 2. Comparison of Measured and Predicted Sorption Percent Removal

Compound	Experiment	Measured Removal (%)	Predicted Removal[a] (%)	Difference[b] (%)
Phenol	SP-3	4.6	3.0	1.6
	SP-4	5.8	4.1	1.7
	SP-5	3.9	2.5	1.4
	SP-6	1.3	2.7	-1.4
1,4-Dichlorobenzene	SP-1	43.0	61.9	-18.9
	SP-2	30.0	56.4	-26.4
	SP-10	72.7	72.0	0.7
	SP-11	78.7	72.4	6.3
Pentachlorophenol[c]	SP-7	86.9	85.1	1.8
	SP-8	76.9	81.2	-4.3
	SP-9	97.2	92.7	4.5
	SP-11	92.2	89.0	3.2

[a](initial concentration - endpoint concentration) ÷ initial concentration x 100.
[b]Difference = measured removal - predicted removal.
[c]Pentachlorophenol partially ionized at pH = 7, $K_{ow} = 7700$.

Table 3. Comparison of Measured and Predicted Loading for Sorption Batch Experiments

Compound	Experiment	Measured Loading (mg/g)	Predicted Loading[a] (mg/g)	Percent Deviation
Phenol	SP-3	0.8	0.5	37.5
	SP-4	0.7	0.5	28.6
	SP-5	0.8	0.5	37.5
	SP-6	0.3	0.5	-66.7
1,4-Dichlorobenzene	SP-1	6.7	9.7	-44.8
	SP-2	9.8	18.4	-87.8
	SP-10	7.9	7.8	1.3
	SP-11	2.7	1.9	29.6
Pentachlorophenol[b]	SP-7	1.6	1.6	1.9
	SP-8	2.0	2.1	-4.0
	SP-9	1.4	1.3	5.0
	SP-11	1.7	1.7	0.6

[a]C_s Values
[b]Pentachlorophenol partially ionized at pH = 7, $K_{ow} = 7700$.

oxidized and stripping losses below detectable limits. Approximately 56% of the feed ^{14}C phenol was recovered as $^{14}CO_2$ for both compounds. Removal of these compounds from activated sludge units by sorption is insignificant on a material balance basis, with average compound loadings of <84 μg/g MLSS and 28 μg/g MLSS determined for phenol and aniline, respectively.

Biological oxidation was also determined to be the major removal mechanism for the toluene, the most volatile of the test compounds. Approximately 67% to 70% of the feed toluene ^{14}C was recovered as $^{14}CO_2$ and only 5% to 6% of the ^{14}C was recovered as soluble metabolites. The ability of the activated sludge systems to biologically degrade toluene was found to be very sensitive to deviations from steady-state operating conditions (flow fluctuations, etc.). Grab samples of mixed liquor indicated variations in the concentration of toluene in the aqueous phase to range from <0.05 mg/L to 4.7 mg/L.

Pentachlorophenol was found to be extremely resistant to biological oxidation and stripping. Sorption onto sludge was determined to be the major removal mechanism, with both ^{14}C analyses and pentachlorophenol analysis indicating that 6% to 8% of the feed pentachlorophenol was removed through sorption to waste solids. The average pentachlorophenol loading on biological solids was determined to be 1967 μg/g MLSS and 1801 μg/g MLSS for reactors 1 and 2, respectively.

The predictive fate method, which was developed for stripping, was determined to be accurate in predicting the concentration of test compounds in the vent gas as a function of the measured concentration in the aqueous phase, the Henry's law constant, and the relative air flow/liquid volume ratio. Vent gas concentrations of toluene predicted from daily average data were within ±50% of observed values for approximately 70% of the observations. The remaining observations had either or both vent gas and/or mixed liquor concentrations below the detection limit.

Average loading of aniline, phenol, and pentachlorophenol onto biological solids were found to be related to the octanol-water partition coefficient. However, the proposed predictive equation for relating equilibrium loading to the equilibrium aqueous phase concentration was found to predict loadings that were lower than those observed for aniline, an ionizable

compound. Conversely, predicted pentachlorophenol loadings were seven-fold higher than those observed.

Overall Mathematical Predictive Fate Method

An overall mathematical PFM was developed to predict the equilibrium aqueous phase concentration in the secondary effluent from a completely mixed activated sludge system. The stripping PFM and the equilibrium sorption PFM for substrates at low concentrations are incorporated into traditional "uniform biomass" design models taken from environmental engineering. This equation, and its derivation, is given in the project report.

Conclusions

This work represents a broad overview assessing the feasibility of using both experimental and mathematical predictors to quantitatively determine fates. Methodology using chemical engineering kinetic approaches and reactor-design equations appears to be a viable way to analyze multi-mechanism processes for various reactor configurations.

The data base existing at the beginning of this effort was limited because of the specific emphasis given to different questions in each study and to the past focus on removal as opposed to specific chemical fates. Some indications on relative fate processes may still be drawn, particularly from more recent studies that look at numerous compounds with the same experimental protocol.

Stripping in completely mixed, diffused air systems has been found to be essentially an equilibrium process, and predictive equations are proposed. Verification on other compounds and system configurations is suggested. The effects of contaminants (surfactants, salts, oils, and nonviable biomass) are significant on oxygen transfer rate constants and less significant on stripping transfer processes. Stripping rate estimates based on oxygen transfer rates for contaminated waters such as treatment plant mixed liquors must be questioned.

Sorption was quantified in a variable-volume batch reactor using nonviable biomass and later in continuous laboratory activated sludge studies. An equilibrium deterministic predictive equation is proposed for low aqueous concentrations. Kinetic sorption rates for the compounds studied could not be quantified because of their rapidity compared with the time required for sampling and analysis.

Numerous kinetic rate constants for biological processes exist and can be formulated. Each of these rates applies to specific cases in substrate and biomass concentration and reactor configuration. Little reliable data exist in this area, and accepted overall methodologies are lacking. First- and second-order (first order in both substrate and biomass concentration) rate constants are developed in this study for batch, fill-and-draw, and continuous reactor configurations for the compounds studied. Disappearance rates were calculated, but mineralization rates were emphasized. Mineralization provides an unambiguous predictor of biodegradation, but disappearance kinetics are required for fate predictive equations. Mineralization rates for the compounds studied were generally comparable over the batch, fill-and-draw, and continuous reactor configurations. However, disappearance rate kinetics were comparable only for batch and fill-and-draw systems and ranged from 2 to 3 orders of magnitude slower than those demonstrated in the steady-state continuous systems. The batch and fill-and-draw kinetic disappearance values are of the same order as data reported in the literature for specific compounds and BOD.

Laboratory-scale activated sludge systems were designed and operated to elucidate compound fates in a conclusive fashion. This included the use of radiolabeled substrate in conjunction with nonlabeled substrate and sampling of all streams of fate importance. Many of these procedures are substantially more difficult to implement in full-scale processes. Full-scale fate data cannot, therefore, be as precise or conclusive as the more controlled experiments.

A coupled, algebraic, predictive fate equation is presented subject to assumptions and derivations given in the project report. An example of organic compound fates is provided by assuming most probable, maximum, and minimum values for the equation variables and using biological rate constants calculated from other studies. Generally, the most probable values agree with the findings in this study, and the ranges agree with full-scale plant studies implemented by EPA.

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